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STUDY OF MINERAL FINES IN TAR SAND BITUMEN AND THEIR ACID SENSITIVITY  
USING EPR AND FTIR TECHNIQUES

By

V. M. Malhotra\* and W. R. M. Graham  
Department of Physics, Texas Christian University, Fort Worth, Texas 76129

INTRODUCTION

The recovery of oil from tar sand deposits by conventional techniques is not possible because of the high viscosity of the bitumen. Processes which have been suggested for the *in situ* recovery of this heavy oil all require thermal and water injection treatment. Clementz (1) has found that asphaltenes are rapidly and irreversibly adsorbed on smectite, kaolinite and illite under near anhydrous laboratory conditions. Based on this observation, he has suggested that the adsorption of petroleum heavy ends on clay minerals would result in their stabilization against dispersion and subsequent migration. Since clay particles coated with heavy ends may be oil wettable, they may readily enter the oil phase, resulting in poor recoveries. The presence of minerals in conventional oil reservoir formations can reduce permeability and obstruct flow either by the expansion of smectite and illite clays to fill pore spaces or by the dispersion and lodging of very small amounts of clays in restrictions.

Recent results from studies on bitumen, extracted with benzene, from Utah (2) and Athabasca (3) tar sands have shown that it is impossible to remove coated clay particles from the bitumen, even when it is subjected to severe centrifuging conditions. Studies on tar sands which provide information on potential oil wettable minerals and the minimization of their negative effects on recovery are, therefore, of substantial importance.

EXPERIMENTAL PROCEDURES

The tar sand sample used in this study originated from the P. R. Spring Outcrop NE Sec. 32, T-Z5-1/2S, R23F, Uintah County, Utah, and was supplied by the Laramie Energy Technology Center through the courtesy of Dr. J. F. Branthaver. Free bitumen was separated from the heavy minerals in the raw tar sand by a Soxhlet extraction technique (4) using benzene as the solvent. Fine clay particles were observed to escape through the thimble during extraction; these could be removed only by further treatment. A 10% solution of bitumen redissolved in benzene was centrifuged at  $8000 \text{ rev min}^{-1}$  for 35 min at 277 K, and then decanted. The fine clay particles remaining at the bottom of the tube were washed repeatedly with benzene until the solution was colorless in order to remove any remaining free bitumen. This centrifuged mineral residue (CMR) was the object of the present study.

Electron paramagnetic resonance (EPR) spectra were recorded with a Varian V4500 spectrometer operating at 9.2 GHz with 100 kHz magnetic field modulation. A Varian V-4557 variable temperature accessory was used in recording spectra at temperatures as low as 80 K. The sample temperature was continuously monitored by a chromel-constantan thermocouple attached to the sample tube.

Infrared spectra of samples prepared in KBr or CsI pellets and Nujol mulls were recorded in the range  $4000\text{--}225 \text{ cm}^{-1}$  using a Nicolet 5DXE Fourier transform infrared (FTIR) spectrometer and a Beckman 4250 dispersive spectrometer.

RESULTS AND DISCUSSION

FTIR

The IR spectrum of the CMR shown in Figure 1 exhibits absorptions at  $3000\text{--}2800$ , 1710, 1600 and  $1500\text{--}1350 \text{ cm}^{-1}$ , thereby providing evidence that bitumen remains after Soxhlet extraction, probably in the form of free bitumen which has not been adsorbed on mineral surfaces and also as

\* Present address: Department of Physics, The University of Calgary, Calgary, Alberta  
Canada T2N 1N4

bonded bitumen in mineral-organic complexes. The observation of a decrease in intensity of the 3000-2800 and 1500-1350  $\text{cm}^{-1}$  bands on further treatment of the CMR with benzene indicates that additional free bitumen has been removed. A further reduction in the intensity of these bands when the stronger, chloroform-acetone (70:30) solvent is subsequently used, suggests that, in this step, adsorbed bitumen has been partially removed. In contrast to the aliphatic bands, the carbonyl and aromatic bands at 1710 and 1600  $\text{cm}^{-1}$  are unaffected by the solvent treatment. This behavior indicates that stable complexes of these functional groups are formed with the mineral matter and are thus resistant to solvent extraction.

Utah tar sands consist of complex mixtures of organic matter and mineral material in which the sand grains are completely encompassed by bitumen. In contrast, the individual grains in the Athabasca deposits are surrounded by a thin water film. In the P. R. Spring deposit, which is of the consolidated type, bitumen is in direct contact with and bonded to the mineral particles.

Although a detailed study of the minerals present in P. R. Spring tar sands has apparently not been reported, quartz grains, mica flakes, calcite and clay particles were recognizable in the mineral fraction remaining after bitumen extraction and clays would be expected to be the major constituent of the CMR. IR and, more recently, FTIR spectroscopy have proved to be invaluable in the identification both of functional groups and of minerals in coals (5) and tar sands (2, 3). Figure 1 shows the spectrum of the CMR recorded in the ranges 4000-2000 and 1800-225  $\text{cm}^{-1}$ . Typical, prominent carbonate features (6) include a broad band in the 1400-1500  $\text{cm}^{-1}$  region and sharper bands at  $\sim 870$  and 720  $\text{cm}^{-1}$ . Treatment with dilute  $\text{H}_2\text{SO}_4$  of a sample of the CMR fraction which had been cleaned with a chloroform-acetone solution resulted in the complete removal of the 1450  $\text{cm}^{-1}$  band, in agreement with the assignment of this band to carbonates. Si-O vibrations are responsible for broad bands in the 900-1100  $\text{cm}^{-1}$  region and sharper features in the 700-800 and 400-530  $\text{cm}^{-1}$  regions. Characteristic quartz features are strong, broad bands at 1172 and 1082  $\text{cm}^{-1}$ , originating from Si-O stretching modes, as well as bands in the vicinity of 460  $\text{cm}^{-1}$  from Si-O bending vibrations.

The IR spectra show that the CMR, as expected, consists principally of a mixture of clays (7). The presence of kaolinite can be discounted, at least at concentrations  $>1\%$ , because of the absence of the higher-frequency member of the characteristic pair of O-H stretching bands at 3694 and 3620  $\text{cm}^{-1}$  (8). The single band at 3620  $\text{cm}^{-1}$  is characteristic, however, of smectite and illite clays. As shown in Figure 1, other typical bands of these clays are also observed. The very broad band at 3400  $\text{cm}^{-1}$  and the sharper band at 1625  $\text{cm}^{-1}$ , which are O-H stretching and bending vibrations, respectively, are attributable to the loosely bound, interlayer water contained in smectite or hydrous illite. The broad band at  $\sim 3200$   $\text{cm}^{-1}$  is characteristic of water molecules tightly bonded to particle surfaces in a monolayer. Weak bands appearing at 835 and 795  $\text{cm}^{-1}$  are (Al, Mg)-O-H vibrations which can be assigned to smectite. Clays also absorb strongly at 900-1100  $\text{cm}^{-1}$ , but overlapping bands in this region prevent analysis of these features in detail.

A further diagnostic test was made in order to verify the identification of smectite by forming a complex with 2,2'-dipyridyl, which is specific to smectite clay and results in a band at 1435  $\text{cm}^{-1}$  (9). For this test, the CMR was treated with a chloroform-acetone mixture and then with dilute  $\text{H}_2\text{SO}_4$  and HCl acid to remove carbonate minerals. After drying for 24 h at 383 K, the sample was ground for 15 min with 2,2'-dipyridyl and ethanol in a steel ball mill vibrator, washed with ethanol to remove any unreacted 2,2'-dipyridyl, and air dried. A KBr pellet was made and the FTIR spectrum shown in Figure 2 was recorded. The appearance of a band at 1435  $\text{cm}^{-1}$  confirms the presence of smectite clay in the CMR fraction. The close similarity of the IR spectra of illite and smectite clays precludes further, detailed analysis; however, based on the preceding discussion it can be concluded that these clays along with carbonates are undoubtedly the principal constituents of the CMR.

### EPR

The EPR spectrum of the CMR shown in Figure 3(a) exhibits four main features: (a) an intense broad signal at  $g \approx 2$  which is probably due to iron oxide and/or hydroxide, either in the form of discrete particles or on the surface of illite and smectite clay particles, (b) a partially resolved, six-peak signal typical of  $\text{Mn}^{2+}$  which is superimposed on the broad signal, (c) a sharp line at  $g \approx 2.003$  which can be assigned to organic free radicals, and (d) an absorption at  $g \approx 4.3$  characteristic of  $\text{Fe}^{3+}$  at sites of rhombic symmetry.

The intense, broad signal at  $g \approx 2$  is probably due to  $\text{Fe}_2\text{O}_3$ . A similar spectrum has been observed by Griscom and Marquardt (10) for finely ground ferrites in lunar soil samples and attributed to the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . EPR spectra of the CMR following treatment with either  $\text{H}_2\text{SO}_4$  or HCl acid and of the acid extract (see Figure 3(b)) show that the broad signal has largely disappeared from the CMR spectrum, confirming that it originates with adsorbed or free iron oxide.

The six-peak spectrum superimposed on the  $\text{Fe}_2\text{O}_3$  spectrum at  $g \approx 2.0$  is characteristic of  $\text{Mn}^{2+}$ ; here the site is expected to be in carbonates or clays. Since drying the CMR at temperatures

up to 573 K had no effect on the spectrum, the possibility that it originates with hydrated  $Mn^{2+}$  in smectite clays (11) can be ruled out. Malhotra and Graham (12) have reported a well resolved hyperfine spectrum of  $Mn^{2+}$  in coal-derived calcite. The partly resolved, smeared appearance of the spectrum may indicate that  $MnCO_3$  is responsible, since, in that case, broadening of the hyperfine lines because of dipolar interaction is expected. Treatment with dilute HCl or  $H_2SO_4$  acid resulted in the removal of the  $Mn^{2+}$  signal from the CMR spectrum and the appearance of a well resolved spectrum in the acid extract (Figure 3(c)). This behavior is consistent with the assignment to  $MnCO_3$ . Shepherd and Graham (13) have observed an EPR spectrum of  $Mn^{2+}$  at two sites in the mineral fraction of a sample of Circle Cliffs tar sand; however, detailed analysis of that spectrum shows that the  $Mn^{2+}$  occurs in dolomite.

When the CMR was treated with large quantities of a chloroform-acetone solution, the sharp, isotropic line at  $g \approx 2.0028$  was reduced in intensity while the  $g$ -value and line-width were unaffected. This behavior is consistent with its assignment to organic free radicals and rules out the possibility of the cause being a defect in the smectite or illite clay structures. A detailed study of the application of the EPR technique to free radicals in P. R. Spring tar sand has been reported elsewhere by Malhotra and Graham (4). The downward shift in  $g$ -value from 2.0034 to 2.0028 and the increase in linewidth (see Table I) observed for the CMR in comparison to free bitumen reflects the selective removal of certain organic fractions during Soxhlet extraction. Treating the CMR with dilute  $H_2SO_4$  reduces the linewidth and indicates further, selective removal of organic fractions. The  $g$ -values and linewidths for P. R. Spring organic fractions and for the CMR are summarized in Table I. Since  $g$ -values for aromatic hydrocarbons are typically 2.0026-2.0028, but higher for heteroatomic  $\pi$ -electron radicals, it is likely that the former contribute to the CMR free radical signal. As noted earlier, the persistence of the  $1600\text{ cm}^{-1}$  aromatic band in the FTIR spectrum even after the CMR fraction was subjected to various treatments, suggests that the aromatic groups are strongly bound to the surfaces of the illite and smectite clays. These observations are, thus, consistent with the report by Clementz (1) that aromatic fractions are selectively adsorbed on clays. A bitumen covering on clay particles would render them hydrophobic and, hence, they may readily enter the bitumen phase during *in situ* recovery processes.

TABLE I

FREE RADICAL EPR PARAMETERS FOR P. R. SPRING TAR SAND FRACTIONS

Sample	$g$	$\Delta H$ (mT)	Reference
Bitumen	2.0034	0.53	4
Petrolene	2.0035	0.57	4
Asphaltene	2.0034	0.54	4
CMR <sup>a</sup>	2.0028	1.33	Present work
CMR treated with $H_2SO_4$	2.0027	0.63	Present work
CMR treated with acid and washed with chloroform-acetone	2.0031	0.69	Present work

a. Centrifuged mineral residue.

Many clay minerals and carbonates common to hydrocarbon fields contain iron which is released when the minerals are dissolved in the acids which are used to treat oil fields (14). Released iron forms a ferric gel which blocks pores and reduces permeability; consequently, it is important to know the amount of iron released. If, as suggested by Clementz, treatment with heavy ends of oil is used to stabilize formation, it is of interest to know the effect of acids on bitumen coated minerals during subsequent treatment.

The EPR spectra at 25-275 mT of the CMR residue following treatment with 1N  $H_2SO_4$  and the acid extract appear in Figure 4. The signals at  $g \approx 4.3$  and 9.5 originate with  $Fe^{3+}$  at octahedral sites of rhombic symmetry (15). Of the clays, kaolinite can be disallowed since EPR spectra of both natural and synthetic kaolinites exhibit 3 lines in the vicinity of  $g \approx 4$  (16, 17). This finding differs from the results for the centrifuged residue from an Athabasca asphaltene in which kaolinite has been reported as the major clay constituent (3), but is consistent with the IR results which, as has been noted, indicate no evidence of kaolinite in the P. R. Spring sample. The observed powder pattern spectra were fitted to the spin-Hamiltonian

$$H = g\beta H \cdot S + D[S_z^2 - \frac{1}{3}S(S+1)] + E[S_x^2 - S_y^2] \quad 1)$$

where the first term is the Zeeman splitting, the second and third terms represent the axial and rhombic components of the zero field splitting and  $S=5/2$  and  $I=0$  for  $\text{Fe}^{3+}$ . The derived spin-Hamiltonian parameters shown in Table II for comparison with results for various clays indicate that the observed  $\text{Fe}^{3+}$  EPR spectrum arises from illite (16) and smectite (18) clays. The EPR spectrum of  $\text{Fe}^{3+}$  in the  $\text{H}_2\text{SO}_4$  gives a measure of the iron released by the acid treatment and may be of potential use as a diagnostic tool in determining the amount of iron released when formations are treated, from the EPR spectrum of core samples.

TABLE II  
EPR SPIN HAMILTONIAN PARAMETERS FOR  $\text{Fe}^{3+}$  IN P. R. SPRING CMR<sup>a</sup> SAMPLES  
AND VARIOUS CLAYS

Sample	g	$\Delta H$ (mT)	$\lambda = E/D$	Reference
P. R. Spring CMR	$\sim 2$ $\sim 4.3$	91		Present work
P. R. Spring CMR	4.18	21.7	$\sim 0.333$	Present work
$\text{H}_2\text{SO}_4$ treated	9.65	16.3		
P. R. Spring CMR	4.32	14.3	$\sim 0.333$	Present work
$\text{H}_2\text{SO}_4$ extract	9.65	8.2		
Kaolinite Clay				
Center I	4.2		0.333	16, 17
Ila	4.9			
Iib	$\begin{cases} 3.5 \\ 3.7 \end{cases}$		$< 0.333$	
Mica	4.17 4.29		0.333	15
Smectite	4.33 9.6		0.333	18

a. Centrifuged mineral residue.

A complex spectrum, observed at  $g \approx 1.99$  for a sample of CMR from which  $\text{Fe}_2\text{O}_3$  and carbonates had been removed by acid treatment, exhibited eight peaks characteristic of a vanadyl complex and is similar to spectra observed for Athabasca and Boscan asphaltenes. The CMR and Boscan spectra are shown in Figure 5. Vanadyl is known to occur in a wide variety of carbonaceous deposits in both porphyrin and non-porphyrin complexes (19, 20). The spectrum was fitted to the axially symmetric spin Hamiltonian

$$H = \rho [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (2)$$

where  $A_{\parallel}$  and  $A_{\perp}$  are the parallel and perpendicular hyperfine constants. The derived EPR parameters are shown in Table III together with the spin-Hamiltonian parameters for various vanadyl porphyrins and  $\text{VO}^{2+}$  in  $\text{Mg}^{2+}$ -hectorite clay,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Comparison indicates that the presence of  $\text{VO}^{2+}$  in porphyrins is unlikely and the observation that the vanadyl complex is not removed on treatment with  $\text{H}_2\text{SO}_4$  implies an inorganic environment. The derived parameters are in better agreement with the data for inorganic complexes, particularly in the case where  $\text{VO}^{2+}$  is doped into  $\text{Mg}^{2+}$ -hectorite at the 5% level (22). The observation that the spectrum can be removed by bonding with HCl further supports the tentative suggestion that  $\text{VO}^{2+}$  is in clays. These results for P. R. Spring tar sand are in marked contrast to a study of a sample of Circle Cliffs tar sand in which vanadyl porphyrin has been identified, but no evidence has been found for  $\text{VO}^{2+}$  in inorganic fractions (13).

## CONCLUSION

The results from this work suggest that the EPR and FTIR techniques are important tools in the study of fine clay particles in tar sand and petroleum deposits and have application in understanding the role of clays and their effect on recovery processes.

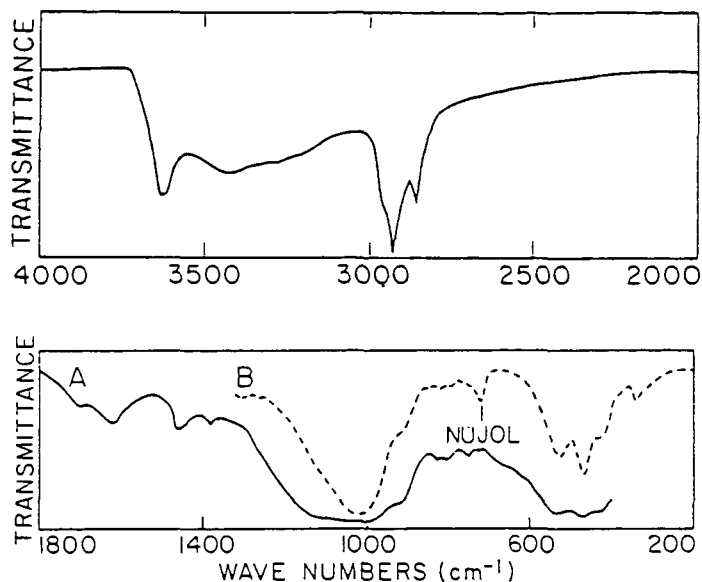


Figure 1. IR spectra of the centrifuged mineral residue in the 2000-4000 and 1800-200  $\text{cm}^{-1}$  regions.

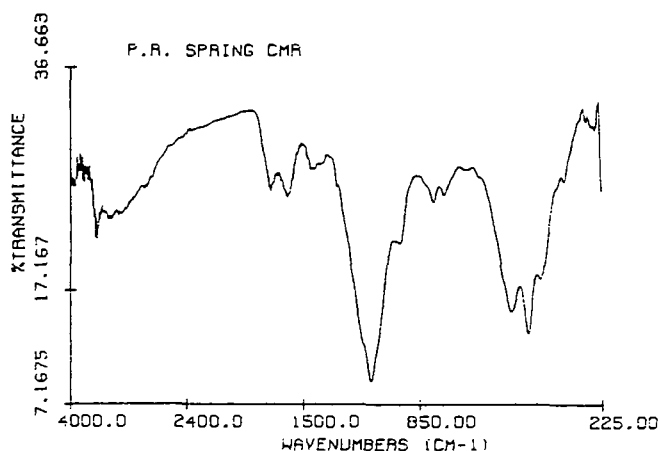


Figure 2. FTIR spectrum of centrifuged mineral residue which had been washed with acetone and chloroform-acetone, and then treated with 2,2'-dipyridyl showing the appearance of the 1435  $\text{cm}^{-1}$  band which is specific to the formation of a complex between 2,2'-dipyridyl and smectite.

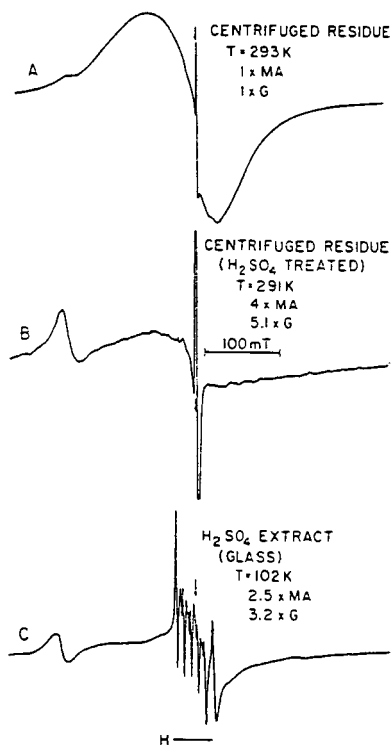


Figure 3. EPR spectrum of (a) the centrifuged mineral residue, (b) the CMR following treatment with dilute  $\text{H}_2\text{SO}_4$  and (c) a glass of the acid extract. MA = modulation amplitude. G = gain.

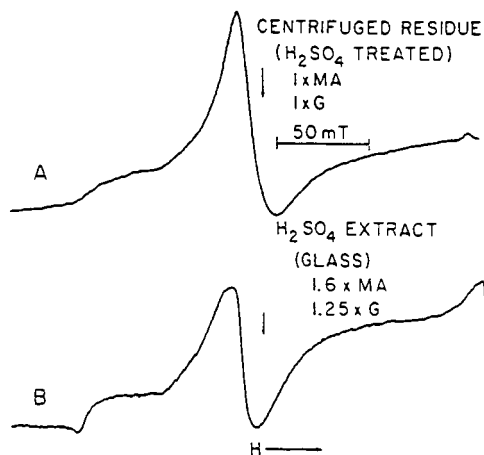


Figure 4. EPR spectra of (a) acid treated EMR and (b) its acid extract in the 25-275 mT region.

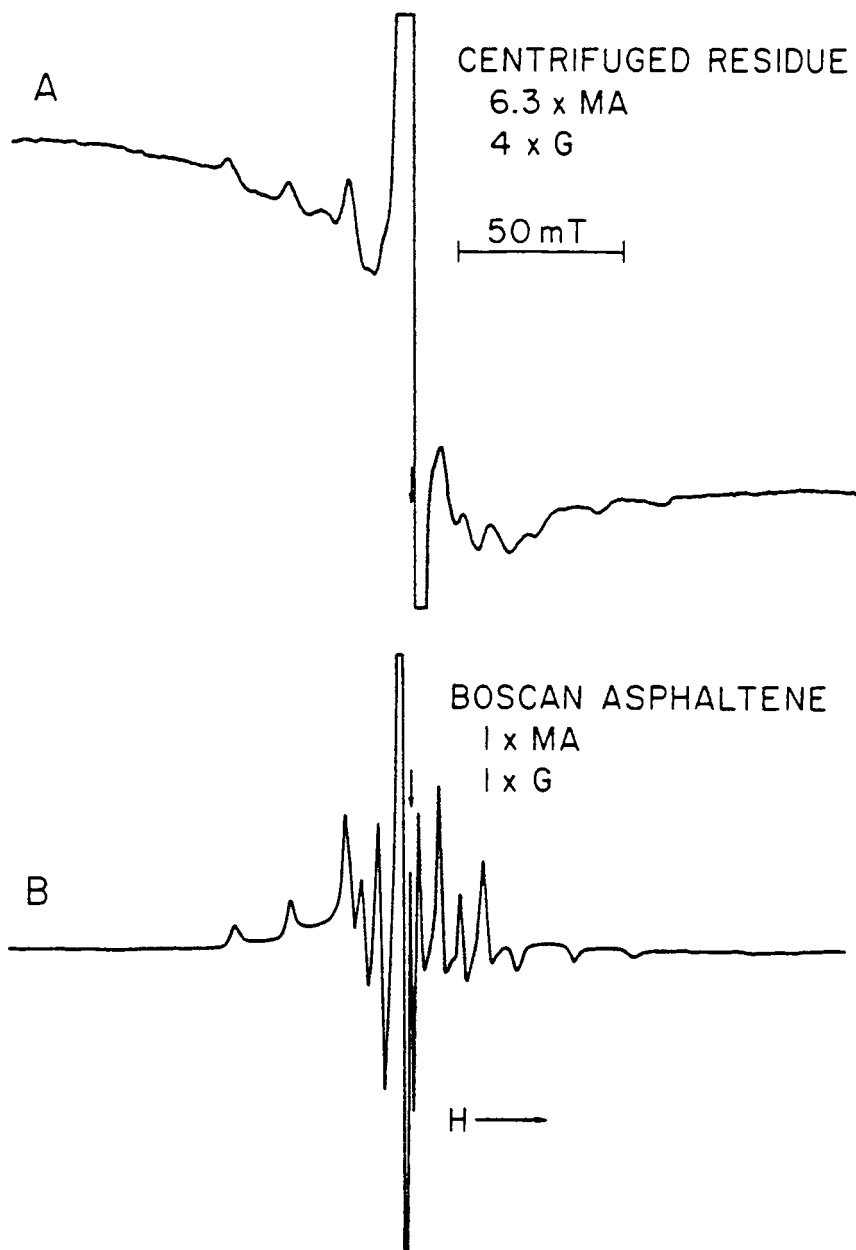


Figure 5. The EPR spectrum of (a) acid treated CMR and (b) Boscan asphaltene.

TABLE III

EPR PARAMETERS FOR  $\text{VO}^{2+}$  IN P. R. SPRING CHAR<sup>a</sup> AND VARIOUS MINERALS

Sample	$g_{\perp}$	$g_{\parallel}$	$A_{\perp}$ (mT)	$A_{\parallel}$ (mT)	Reference
P. R. Spring CHAR	1.9928	1.9432	7.26	18.51	Present work
Boscan asphaltene	1.9861	1.9598	5.93	17.30	Present work
Etioporphyrin I	1.987	1.948	5.61	17.48	19
Etioporphyrin II	1.9823	1.9590	6.13	17.17	21
$\text{Mg}^{2+}$ -hectorite (5% $\text{VO}^{2+}$ )			7.1	19.4	22
- $\text{Al}_2\text{O}_3$	1.989	1.916	7.08	18.12	23
$\text{SiO}_2$	1.982	1.922	7.72	19.51	23

a. Centrifuged mineral residue.

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